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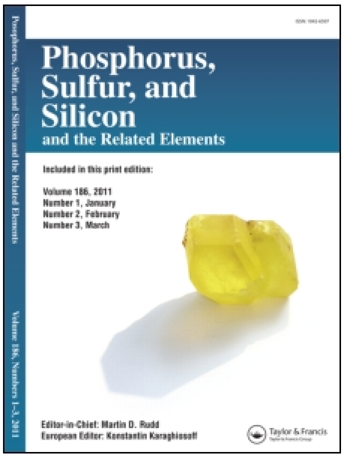

Phosphorus, Sulfur, and Silicon and the Related Elements

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FOREWORD

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FOREWORD

It is not sufficient to know the truth one has to proclaim it.

Louis Pasteur, 1885

The Fourth International Symposium on Inorganic Ring Systems, IRIS-IV, was held at the Faculty of Science of the University of Paris-Sud (Orsay) from 2 to 6 September 1985; it was a continuation of the four preceding meetings: IRIS-I (Besançon, France, 1975), IRIS-Ib (Madrid, Spain, 1977), IRIS-II (Göttingen, FRG, 1978) and IRIS-III (Graz, Austria, 1981).

The specific characteristic of inorganic ring systems is, of course, the absence of the element carbon, which excludes them from organic chemistry. Moreover, their electronic structure is different from that of organic ring systems and obeys generally the law of Dewar, i.e. exhibits a discontinuous electronic structure in the ring in the form of Dewar islands. This results in a significant increase of the transannular bond, whereas in organic ring systems the electronic distribution is often homogeneous and transannular bond energy is negligible.

It is quite difficult to promote a new field of science, especially when the new ideas are contrary to acquired habits and come to affect an old science, such as inorganic chemistry. This problem arose thirty years ago, when the term inorganic ring systems was used for the first time, producing at the time some astonishment, some reservations and even some hostility among chemists. To date, the situation is quite favorable and the work and publication of some forty chemists of various nationalities have shown the reality of our research and the scientific interest in our fight to promote a new field of inorganic chemistry neglected or forgotten for about a century and a half.

It is sure that before new inorganic ring molecules were built by chemists in their laboratories, ring systems were already existing in nature. A typical example is that of native sulfur or crystallized sulfur made up, as we now know, of ring systems with eight sulfur atoms. Selenide, Se_2S_6, is a natural inorganic heterocycle and various silicates of the bentonite type also belong to this class of natural inorganic ring systems. As a matter of fact, our first researches in this field in 1947 were concerned with natural sulfur (reaction of J. Casares). Twenty years later, in 1967, we tried unsuccessfully to organize, in collaboration with our colleague and friend Professor Wannagat, the first international meeting on inorganic ring systems which was to be held in Germany. Our second attempt to organize a first symposium in England in 1970 in collaboration with Professor Heal from Belfast was also unsuccessful. Finally, we succeeded in holding our first meeting in June 1975 at the Faculty of Sciences of the University of Besançon, France. This first meeting was a great success, but it is clear that a synopsis of the work done in this field over nearly 150 years could not be realized in four days. It was decided at the end of this meeting that a second symposium would be held in Gottingen (IRIS-II, 1978) and Madrid (IRIS-Ib, 1977). These were followed by IRIS-III in Graz (Austria) in 1981 and by IRIS-IV in Orsay (France) in 1985.

IRIS-V is scheduled for 1988 in the U.S. at the University of Massachusetts, Amherst, Chairman Prof. Robert R. Holmes.

HISTORICAL REVIEW

From a general point of view, we think it is useful to remember that chemistry as a science does not date back more than two centuries. The origin of chemistry is very old and related to the use of pigments for rupestral paintings and later to the manufacture of glass, enamels, ceramics, to metallurgy, which was already known 400 years B.C., and to the preparation of dyes for fabrics (murex), perfumes, cosmetics, lime mortars etc...

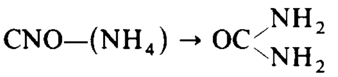
A science is in fact a sum of experimental facts related to each other by a theory which explains them logically. The discovery of new experimental facts leads to an extension of the theory which must take them into account. Sometimes the theory proves to be false, but it has led, nevertheless, to significant discoveries.

To explain the results obtained in chemistry, a doctrine began to develop slowly aι the beginning of the Christian era which is known under the name of alchemy. This name originates from the Egyptian term chema which means earth, to which is attached the prefix al of arabic origin. This term appeared together with the term chemistry in the course of the third century. According to some manuscripts, it seems that the "Chema" was a sacred book containing pharmaceutic, metallurgical and astrological recipes transmitted by Jehovah to the Jewish people, one of the holders of which would have been the famous Mary the Jewish to whom is imputed the discovery of the water-bath. Alchemy had two aims: first, to try to explain the nature of matter by means of theories, such as the phlogiston theory, the theory of the four elements (earth, water, air, fire) and, on the other hand, extravagant objectives, such as the transmutation of metals in the hope of obtaining gold or silver, or the search after the philosophers' stone and the elixir of life. The phlogiston theory was definitively demolished by the experiments of Lavoisier in 1776. The vain attempts of the alchemists during many centuries to transmute metals led, however, to a significant development of knowledge in chemistry and to the isolation of elements such as phosphorus, brass (which looks like gold), oil of vitriol, spirit of salt, aqua regia. Compounds, such as alcohol, alkalies, and borax, were isolated by Arab alchemists, as well as by the famous Geber, Albert the Great, Roger Bacon, Brandt, Basile Valentin, Paracelsus, Libavius, Glauber, Saint Thomas Aquinas, and Casciorolo whose names are often to be found in books on chemistry. After this long period of obscurantism, experimentation, which was so far considered as unworthy of great minds, prevailed over pure speculation, scholasticism and sterile syllogisms. The authority of Aristotle was attacked and the authority of systematic experiment was definitively established by the work of Lavoisier, Boyle, Van Helmont, Torricelli, Henry Cavendish, etc.

Chemistry is simply defined as the science that investigates the characteristics and properties of simple bodies and defined compounds, the various reactions occurring between them under the influence of various factors, and tries to penetrate their inner nature.

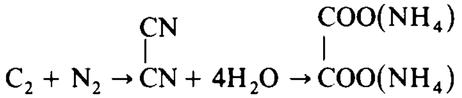
The first purpose of chemical science is to determine the chemical species and to class them into groups of similar properties (analytical chemistry). The second purpose is to transform bodies by appropriate reactions (chemical synthesis) and the third, the most scientific, is to interpret the observations by coordinating them so as to be able to predict from them unknown reactions (theoretical chemistry).

Defined in this way, chemistry covers a very wide field, which is far too wide to be studied as a whole. So, it was divided into sections: first, inorganic chemistry, which became an important scientific branch through the study of the constituent elements of minerals and rocks. Organic chemistry is more recent and its tremendous development does not date back more than 150 years. Scheele (1769–85) discovered tartaric, oxalic and citric acids. Rouelle (1773) discovered urea in the urine. Wray obtained formic acid by distilling ants, Boyle (1675) ethyl nitrate and the hydrocarbons, Sala potassium oxalate (from sorrel). Duchene isolated gluten from flour and Betoletti lactose from milk. These isolated products induced the belief at the end of the eighteenth century that all the substances of vegetable or animal origin were different from those of the mineral kingdom and this led the well-known Novalis in 1772 to give the first qualificative of "organic" to this group of compounds, a term that was definitively sanctioned as Berzelius used it in 1806 to denote as organic chemistry the science of these compounds which were thought to be obtained thanks to the " vital force". This opinion was fully destroyed by Wöhler who succeeded in 1828 in preparing urea from synthetic ammonium cyanate:



$$\mathrm{CNO{-}(NH_4)} \rightarrow \mathrm{OC}\begin{smallmatrix}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{NH_2}\end{smallmatrix}$$

Wöhler prepared, moreover, oxalic acid from synthetic cyanogen:

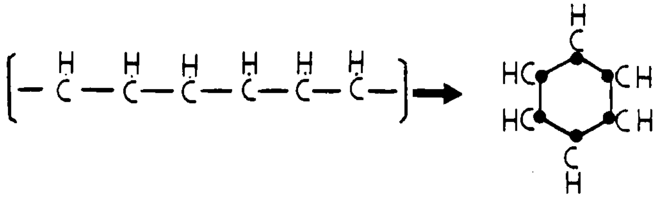


$$\mathrm{C_2 + N_2} \rightarrow \begin{array}{c}\mathrm{CN}\\ |\\ \mathrm{CN}\end{array} + \mathrm{4H_2O} \rightarrow \begin{array}{c}\mathrm{COO(NH_4)}\\ |\\ \mathrm{COO(NH_4)}\end{array}$$

The great German chemist Gmelin established in 1848 in his "Treatise on Chemistry" the difference between organic chemistry or "chemistry of the carbon compounds" and inorganic chemistry, which is concerned with the combinations of all the other elements. This distinction is quite artificial because natural carbonates, such as carbon dioxide, and carbon monoxide are studied in treatises on inorganic chemistry, whereas carbon suboxide is studied in organic chemistry. The study of the reactions between the chemical elements led in the nineteenth century to the notion of valency or saturation capacity. Thus, with hydrogen as the reference atom, oxygen is found to combine with two atoms, nitrogen with three and carbon with four. From the quadrivalency of carbon one is led to the system of formulae of Kekulé (1858). Pasteur (1848) defined in his work on tartaric acids (dextro and levo rotatory and racemic acids) the notion of the asymmetric molecule, which was used by Le Bel and Vant Hoff in their model of the tetrahedral carbon atom to explain rotatory power and isomerization.

The spatial arrangement of the four carbon valencies leads to the notion of chains of carbon atoms which combine with each other and to the notion of the ring, which is very important for our investigations.

The notion of the ring was deduced logically by the German chemist Kekulé and established at the session of 27 January 1865 of the Chemical Society of Paris under the chairmanship of Pasteur and in a famous memoir on the constitution of the aromatic carbides and, in particular, of benzene. This hydrocarbon was peculiar in that in its molecule, C_6H_6, all the carbons and the six hydrogen atoms were equivalent and, consequently, the six $(CH)_6$ groups were identical, which is conceivable only in a closed chain of type:



because an open chain in a hydrocarbon, such as 2,4-hexadiene, with the same formula C_6H_6 has quite different properties:

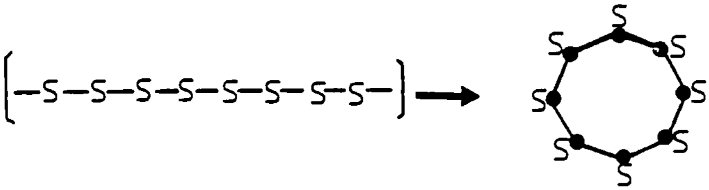
$$H_3C{-}C{\equiv}C{-}C{\equiv}C{-}CH_3$$

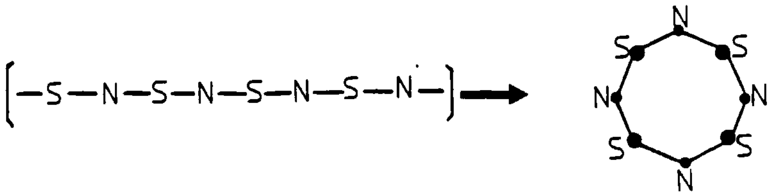
A few weeks later the American Cooper also had the intuition of the cyclic formula of benzene, but the priority of the discovery is accorded to Kekulé. The notion of cycle in organic chemistry thus dates back only a little more than a century.

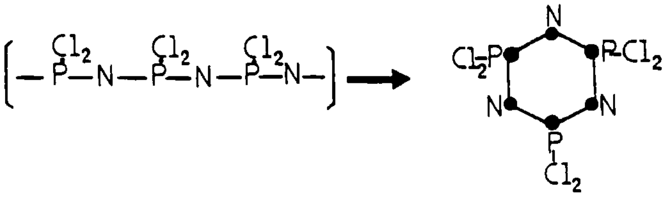
If the cycle only contains atoms of the same type (as in benzene) it is called a homocycle (or isocycle) and if it contains different atoms, such as oxygen, phosphorus, sulfur, etc... it is called a heterocycle.

Till about the year 1940 the terms ring or heterocycle were exclusively applied to organic chemistry, but from this time, thanks to the progress realized in structure determination, it appeared reasonable to conceive molecular ring structures with atoms other than carbon and even excluding this element and, consequently, belonging to the field of inorganic chemistry.

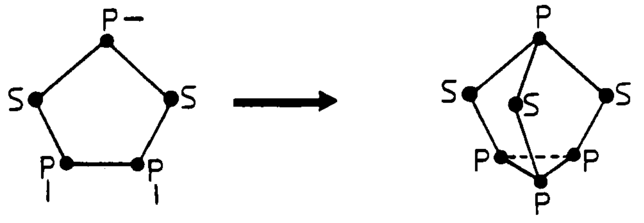
A ring may thus be defined as a chain of atoms limited by ring closure. According to whether the chain is formed by atoms of the same nature or by different atoms we shall have an isocycle or a heterocycle, as below:

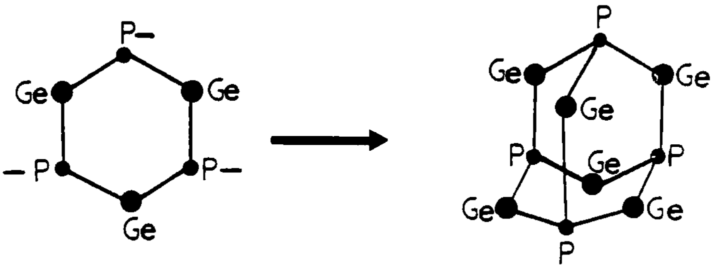






By a similar mechanism, a reduced number of simple cycles may fuse and thus form a closed molecule, which is limited in space by a small number of cycles, as follows:





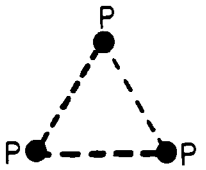
Simple ring compounds, as well as fused-ring compounds crystallize in general in molecular crystals, which proves their similarity and enables them to be distinguished from the linear macromolecules or polyring compounds which are difficultly crystallizable, sparingly soluble in organic solvents, difficultly fusible and chemically very inert, i.e. the very reverse of the molecular ring systems which are very reactive, soluble in organic solvents and low melting.

We have said that inorganic heterocycles are formed by atoms other than carbon. However, in some cases one can admit the presence in the ring of one or two carbon atoms provided that their number is less than that of the other constituent atoms, in order that the ring remains of inorganic type.

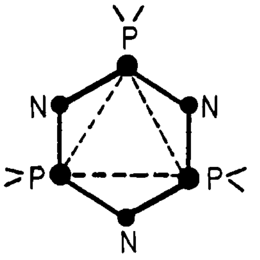
The knowledge of inorganic rings dates from about the year 1809, in which the famous Davy prepared for the first time boranes. Later on, in 1833, the great physico-chemist Thomas Graham prepared cyclophosphates. In 1834 Gregory mentioned the sulfur nitride, N_4S_4, which was prepared by Soubeiran in 1836. Cyclophosphonitriles were prepared by two great German chemists Liebig and Wöhler, but the formula they proposed was not correct, which gave rise to a scientific controversy between the French chemists Laurent and Gerhardt, on the one hand, and the English chemists Stone and Holmes, on the other hand, Finally, Gerhardt succeeded in finding the exact empiric formula ($PNCl_2$) and in 1902 Stokes thought out a cyclic formula for this compound, which was to be brilliantly confirmed in 1939 by radiocrystallography.

Important progress in the study of these compounds was realized after the discovery in 1925 of borazene by Stock and Pohland, which was called inorganic benzene owing to its properties. Chlorosiloxanes were prepared in 1876 by Troost and Haufefeuille, cyclosilazanes in 1948 by Brewer and Haber, the first cyclic thioimine in 1923 by Macbeth and Graham and in 1936 by Arnold.

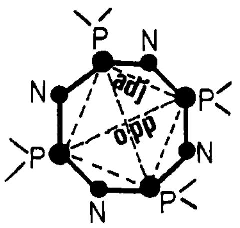
The most significant characteristic of the inorganic heterocycles, which differentiates them from organic rings is the peculiar distribution of the electrons in them. This was studied first by means of quantum mechanical calculations in phosphazenes, then by investigation of the Faraday effect (or magnetic rotational polarization) in the transparency region and it appeared from these investigations that the ring was made up of PNP-islands practically independent of each other, a structure referred to as the Dewar islands model. These results negate the other model suggested by Craig and Paddock, based on the existence of an electron delocalization of benzenoid type. The PNP-islands are independent entities, which give rise to stable rings thanks to the existence in these rings of a transannular bonding interaction of type:



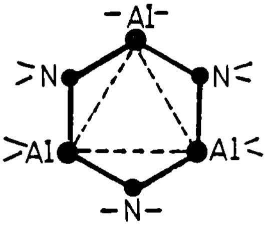
whose energy amounts about to 10% of that of the P-N-bonding, thus explaining the remarkable stability of the trimeric cyclophosphazenes.



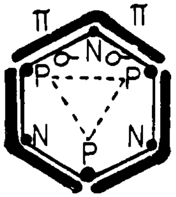
In the eight-membered phosphazenes, two types of transannular bonds exist between the P-atoms: bonding (adj) and antibonding (opp).



These types of bonds are sometimes very important in some inorganic heterocycles, such as the ring compounds S_4N_4 or $(NALH_2Me_2)_3$. In the latter compound, the transannular bonding energy, Al—Al, represents 50% of the bonding energy Al—N of the ring.



The Dewar islands model applies consequently to the most important groups of inorganic heterocycles. The Faraday magneto-optic rotations of the 3,4,5-($PNCl_2$) rings are in the ratio 3, 4, 5, whereas if the electronic structure were of benzoid type the rotation would have varied exponentially with the size of the ring.



On the other hand, Pople has shown that in rings with a benzenoid structure the delocalized electrons give rise under the action of a magnetic field to a current along the ring, i.e. the delocalized π-electrons begin to move freely under the action of the magnetic field applied, thus giving rise to a Pauling-Pople current (strobolic rings), which is, of course, not the case in the Dewar model described above (non-strobolic rings).

H. Garcia-Fernandez
Chairman IRIS-IV. 1985